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(54) Title: STABILIZING CLAYEY FORMATIONS

(57) Abstract

A method of stabilizing a clayey geological formation surrounding a hydrocarbon well is described. It comprises the step of treating the formation with a first reactant and a second reactant, characterized in that a reaction of said first and said second reactant is essentially initiated in the presence of clayey material. The reaction can be characterized by substrate intercalation or condensation stabilization with no pH adjustment or stabilization through epoxide ring opening under neutral or acidic conditions or substrate in–situ polymerization or a combination thereof.

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STABILIZING CLAYEY FORMATIONS

This invention relates to compositions and methods for
stabilizing subterranean clayey formations surrounding a
5 borehole. More specifically, it pertains to clay stabilizing
additives for aqueous fluids used in drilling, completing and
maintaining boreholes.

BACKGROUND OF THE INVENTION

10

When geological formations containing water swelling clays come
in contact with water, particularly fresh water, clays in the
formations may swell and/or disperse with attendant loss of
permeability and/or mechanical strength to interfere with
15 recovery of petroleum or other minerals from the formations.
Swelling and dispersion occur when aqueous fluids used in oil
recovery come in contact with the clays. Clayey formations are
often impermeable or have low permeability or lose part or all
of their permeability on contact of the clays with water or
20 water base systems such as injection fluids, drilling muds,
stimulation fluids and gels. Dispersed clays may also invade a
permeable producing formation during drilling to create low per-
meability zone in the vicinity of the borehole.

25 Given the importance and the ubiquity of clayey or shaley
formations, it is not surprising that much effort has been put
into developing and improving additives for clay or shale
inhibition. Various methods and additives can be found for
example in the United States Patent Nos. 5342530, 5211250,
30 5197544, 5152906, 5099923, 5097904, 5089151, 4842073, 4830765,
4828726, 4563292, 4536303, 4536304, 4536305, 4505833, 4497596,
4172800 and 3578781.

These additives usually are salts and/or polymers which
35 effectively prevent the water from permeating the clay.

Furthermore, it is known to consolidate sandstone and other
highly porous and weak formations with a fluid containing

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polymerizable materials, such as resins or isocyanates in
combination with diols. Those methods are described for example
in the United States Patent Nos.5242021, 5201612, 4965292,
4761099, 4715746, 4703800, 4137971, or 3941191. It is however
5   important to note that the permeability of sandstones and
similar formations differ from those of shale formations by
several orders of magnitude. The consolidation of highly porous,
unstable sandy formations and shale formations with a very low
porosity are therefore generally recognized in the art as
10   separate technical fields.

In technical fields unrelated to the present invention, efforts
to form composites of clayey materials have been described. The
known methods of forming so-called "nanocomposites" include the
15   addition of a reactive (monomeric or polymeric) species to clays
which have been previously treated with another compound with
which it will react. The ensuing chemical reaction can occur in
one of two ways: either the second additive is capable of
physically cross-linking the polymer, or it promotes further
20   self-polymerization. Such processes can result in nanocomposite
silicate-polymers which attain a certain degree of stiffness,
strength and barrier properties with far less ceramic content
than comparable glass- or mineral-reinforced polymers. As such
they are far lighter in weight than conventionally filled
25   polymers.

Examples are provided by the following references: 'Polyamide-
Organoclay Composites', S. Fujiwara and T. Sakamota, Japan,
Patent 51 109,998, 1976; 'Composite Material Containing a
30   Layered Silicate', A. Usaki *et al*, Toyota, U.S., U.S. Patent 4,
889, 885, (1989); M.S. Wang and T.J. Pinnavaia, 'Clay-Polymer
Nanocomposites Formed from Acidic Derivatives of Montmorillonite
and an Epoxy Resin', *Chem. Mater.*, **6**, 468, (1994); T.J.
Pinnavaia *et al*, 'On the Nature of Polyimide-Clay Hybrid
35   Composites', *Chem. Mater.*, **6**, 573, (1994); P.B. Messersmith and
E.P. Giannelis, 'Synthesis and Characterization of Layered
Silicate-Epoxy Nanocomposites,' *Chem. Mater.*, **6**, 1719, (1994);
T. Lan and T.J. Pinnavaia, 'Clay-Reinforced Epoxy

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Nanocomposites, *Chem. Mater.*, **6**, 2216, (1994); E.P. Giannelis,
'Polymer Layered Silicate Nanocomposites', *Adv. Mater.*, **8**, 29,
(1996); T.J. Pinnavaia *et al*, 'Epoxy Self-Polymerization in
Smectite Clays', *J. Phys. Chem. Solids*, 57, 1005, 1996. In spite
5   of the stabilization and strengthening that these additives
impart to the resultant nanocomposite materials, there are
currently several limitations to this technology which are
important from an oilfield perspective. One is that the
established methodology necessarily involves a high-temperature
10 curing process for the chemical reactions to take place; another
is that such an approach inevitably results in the production of
composites in which the silicate is delaminated and randomly
distributed within the polymer matrix. No technology has been
developed which is capable of stabilizing clay silicates under
15 ambient, aqueous conditions.

In view of the above, it is an object of the invention to
provide a novel method of stabilizing subterranean clayey
formations surrounding a borehole. It is another, more specific
20 object of the invention to provide clay stabilizing additives
for aqueous fluids used in drilling, completing and servicing
boreholes under conditions appropriate to drilling oil wells.

25   SUMMARY OF THE INVENTION

This invention is concerned with the identification of a wide
range of compounds which are capable of strengthening and
stabilizing clay and shale minerals through a process of in-situ
30 polymerization. These diverse compounds (or "additives") include
both monomers and polymers, in aqueous solution or suspension.
The resulting nanocomposite materials, which have dramatically
enhanced mechanical properties compared with the original clay
and shale samples, have a vast range of potential materials-
35 science and materials-technology applications both within and
outside the oilfield.

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In chemical terms, the invention comprises a wide variety of
additives which are capable of stabilizing clay films in aqueous
solution. The additives that have been tested encompass four
broad areas: (1) species which are capable of intercalating clay
5   galleries and affording stabilization such as diamines,
polyethylene glycols (PEGs), polypropylene glycols (PPGs) and
polymeric diamines; (2) reagents which are capable of undergoing
condensation reactions and thus polymerizing in-situ such as
diamines, aldehydes, ketones, dicarboxylic acids; (3) reagents
10   which are capable of ring opening of epoxides or acrylates
effecting polymerization in-situ such as alcohols, amines; (4)
reagents which are capable of self-polymerization within clay
galleries such as alkenes. All of these techniques provide
considerable stabilization over untreated films.
15

There are three main applications of the invention. Firstly, it
is envisaged that a drilling mud formulation containing a
combination of the specified compounds described below may be
used as a clay and shale swelling inhibitor fluid, to maintain
20   the integrity of the wellbore during conventional drilling
operations. Secondly, a completion fluid formulation containing
a combination of the same compounds may be used for general
remedial operations in the wellbore. Finally, the invention may
be used to achieve the goal of "casingless drilling", that is to
25   achieve with one and the same drilling and completion fluid the
equivalent result of what is today obtained through a
combination of drilling, casing and cementing operations.

These and other features of the invention, preferred embodiments
30   and variants thereof, and further advantages of the invention
will become appreciated and understood by those skilled in the
art from the detailed description following below.

35   BRIEF DESCRIPTION OF DRAWINGS

FIG 1.   shows the cuttings hardness data for the combinations
              of DAP, DEC, EDA, BNH2 and Glyoxal, together with the

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corresponding results for each of the components on
its own in water.

FIG 2   shows the resulting change in permeability as a
5   reaction in accordance with an example of the present
           invention progresses through a core sample.

EXAMPLE(S) FOR CARRYING OUT THE INVENTION
10
The level of clay stabilization provided by different additives
and formulations were assessed by several laboratory techniques.

All combinations of chemical compounds were initially assessed
15 using thin clay films as the substrate._In this testing
procedure a small piece of montmorillonite clay film is treated
with a combination of reagents which might be capable of cross-
linking or polymerizing inside clay layers and examining the
resulting clay for strength and rigidity in a qualitative
20 manner. The treated films were extracted with chloroform and the
extract analysed by Mass Spectrometry for direct evidence of
polymerisation. The most definitive evidence for polymerisation
was obtained by solid state NMR on films produced from Laponite,
a synthetic clay without the paramagnetic impurities present in
25 the natural montmorillonite clay.

Some of the combinations were then assessed in an outcrop shale,
Oxford Clay, by measuring the permeability change induced in a
shale core and/or the change in hardness of shale cuttings when
30 exposed to the reactive chemistry.

(1) Clay Film Tests

In this testing procedure a small piece of montmorillonite clay
35 film is treated with a combination of reagents which might be
capable of cross-linking or polymerizing inside clay layers and
examining the resulting clay for strength and rigidity in a
qualitative manner.

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All the film tests described below were performed on the same batch of montmorillonite clay films. The films have been stored in a refrigerator in sealed Petri dishes and checked periodically by infrared spectroscopy to ensure integrity of the samples.

A very wide range of potential stabilizers were examined in terms of their chemical reactivity, structure and the conditions under which the tests were performed. All tests have been performed in an identical manner by the addition of a piece of montmorillonite film to an aqueous solution of the intercalator ($5cm^3$ of a 5% w/w solution), the pH of which had already been adjusted (where necessary, with 10% v/v aqueous HCl solution). The potential cross-linking reagent was then immediately added. The intercalating reagents investigated were BNH_2, B2P, B4P, DAP, DEA, EA, EDA, EG, HQ, P, PA, PC, PEDG, PPD, PPDG and STAPLEX650 and the potential cross-linkers A, AA, BA, DEC, DEM, DEO, DIT, DMM, EPP, FS, GA, MA, OA, PPDGE, PO and styrene. Cross-linkers were added as either neat reagents ($0.5cm^3$ A, DEM, DEO, DIT, DMM, EPP, MA, PPDGE, PO, styrene and 0.5g BA) or as aqueous solutions ($5cm^3$ 5% w/w solution AA, DEC, OA; $1cm^3$ of 50% w/w solution GA and $5cm^3$ of a 37% w/v solution FS). Films were then allowed to stand in the reaction mixture for 1 day before washing with distilled water and were then placed in fresh distilled water to monitor their long term stability. (The abbreviations used in this paragraph and the following are listed in Appendix 1.)

The montmorillonite film tests provided a means of ascertaining the potential of a number of reagent combinations; the results are summarized in Table 1 (Appendix 2). (In the table of Appendix 2, the term "Stable" applied to describe the film stability means that such films do not dissolve in water, while "Exfoliates" simply means they are visibly fatter after treatment. The latter term does not mean the films fall apart; this only happens if extreme exfoliation occurs and the resulting material does not have a matrix around it which

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"sets".) These combinations can be broadly divided into four
categories, i.e., (a) Substrate intercalation;(b) Condensation
stabilization with no pH adjustment; (c) Stabilization through
epoxide ring opening under neutral or acidic conditions; (d)
5   Substrate in-situ polymerization.

Physical intercalation of the investigated compounds into the
interlamellar layers of the clay, the clay galleries, is a
condition for the subsequent chemical reactions, as mentioned
10   below under (b), (c) and (d), to occur. Intercalation itself
without chemical reaction, described under (a), is in some cases
capable of enhancing the stability of the clay. However, it is
the subsequent reaction that gives an increased clay stability.

15   (a) Substrate Intercalation

Three films (3, 6 and 24, Table 1) were treated with potential
intercalators without any chemical cross-linking reagent capable
of forming covalent bonds. It was found that by mixing PEG and
20   BNH_2 solutions in equal quantities a very stable film could be
produced. This is consistent with the effect of BNH_2 alone, but
shows considerable improvement on PEG stabilization, indicating
that amines are considerably superior for the stabilization of
clays.
25

(b) Condensation Stabilization

These films are generally the most robust films that have been
produced. Particularly impressive properties being associated
30   with films 1, 7, 34, 37, 40, 42 and 43 (Table 1). These types of
additives are preferred for bore-hole stabilization. In addition
to these treatments, a number of other treatments are available
(films 50, 51, 52 and 53 are particularly stable) and that some
very interesting effects can occur within apparently similar
35   reactant sets; e.g. although EA provides a stable film with DEC
(film 53), the related DEA does not, and the film decomposes
upon soaking in fresh water (film 54). Attempts to produce
polyesters appears to have been less successful (films 55-62).

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However, it is interesting to note that both film 57 and 61 were both very much more robust than any of the other films in this series.

5   The condensation reactions required to provide stabilization in clay galleries involve equilibria between reactants and condensation products. Under aqueous conditions the reactants will clearly be favored, a situation akin to that pertaining in drilling fluids. However, upon intercalation in the
10   interlamellar layer an anhydrous environment is created, through the concomitant expulsion of water. These conditions facilitate the condensation process and lead to film stabilization whilst preventing substrate polymerization in the drilling mud.

15   (c) Ring Opening Stabilization

The chemical process achieved by the ring opening of epoxides is akin to the synthesis of a number of polymers, including e.g. PEG, in which a chain reaction is started after initial ring
20   opening resulting in an *in situ* epoxide polymerization. To produce a stable film, acidic solutions is employed; the acidity of which is dependent upon both the intercalator and the cross-linker. When the diamines (EDA, DAP and BNH_2) are used, only mildly acidic (ca. pH 6) conditions are required with both PO
25   and EPP to produce very robust films (10, 11, 14, 15 and 25-27, Table 1). With PPDGE, much more acidic conditions (pH 2) produce more impressive films (28, 29) than at less acidic pH (films 9, 29). Stable films can be produced by adding a small quantity of a diamine solution to the bulk PEG liquor and treating them with
30   epoxides under mildly acidic conditions (16B and 17). Films can also be stabilized with PEG and all of the epoxides, although more acid conditions (pH 2) are required (30-32); the resultant films are very soft but stable.

35   (d) Substrate in-situ Polymerization

Of the four methods investigated to produce stable films, this has been the least successful. This is perhaps not entirely

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surprising since the polymerisation of a substrate necessitates
a reaction initiator and it is difficult to control this
process. This problem is highlighted by film 12 which resulted
in the entire test solution polymerising. Generally, this
5   reaction type produces exfoliated films (2, 4, 5, 8 and 20),
which are often considerably swollen and blistered, indicating
that the reactions are rapid and too aggressive for the films.
Whether these reactions are of use to stabilise shale is
currently an open question. Clearly, a solution which
10   polymerises, as is the case for 12, is undesirable, but the
stable film produced with EDA and A (film 33) indicates that
there is some potential in this methodology.

15   Evidence for absorption into the interlamellar layer of
substrates

It is important to establish that the reagents are actually
binding within the interlamellar layers of the films rather than
20   merely polymerizing on the film surface. Evidence for an
intercalation effect was established through the use of X-ray
diffraction studies on a number of stable films; see Table 1.
It can be clearly seen that changing the intercalating substrate
changes the d-spacings of the montmorillonite films. What
25   perhaps provides more conclusive evidence of a genuine
polymerization within the interlamellar layer are the range of
d-spacings that are observed for the intercalating substrate,
EDA. Values ranging from 12.72 Å (film 36) to 17.72 Å (film 34)
are observed. Both of these films are stable, flexible and hard
30   and show no signs of exfoliation typical of swelling due to
water viz. marked whitening.

Perhaps even more revealing are the different spacings observed
for the same substrates in films 36-38. Although the treated
35   films all have relatively similar properties (with perhaps most
superior behavior attributable to film 37) the d-spacings are
different. The two films (36 and 38) which have been adjusted to
acidic pH both show similar d-spacings of ca. 13 Å whereas film

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37 (in which unchanged substrates have been employed) shows a d-spacing of ca. 15 Å.

Stability of Treated Films

5   All films that could be, were washed thoroughly with water and then placed in distilled water to investigate their long term stability under saturated aqueous conditions. All of the treated films (1, 7, 10, 14, 16B, 17, 25, 27-43, 50, 52, 57, 61, 63-66)
10   show very impressive stability with only films 31, 32 and 61 showing any signs of decomposition after up to four months. Films 31 and 32 do show some exfoliation but can still be handled quite readily. Film 61, however, is too fragile to handle and decomposes. One interesting effect is observed after
15   prolonged soaking of films treated with EPP. All, with the exception of film 25, become covered with a sticky coating and some (10, 14, 17) become transparent. The sticky coating can be accounted for due to epoxide leaching from the clay and polymerising on its surface. The second effect is more difficult
20   to account for but must relate to a change in the refractive index of the film in some way upon coating with the polymerising epoxide. This effect also substantiates the absorption of substrates into the clay films (hence confirming X-ray diffraction results and extraction studies for 10) as all
25   substrates external to the clay are initially removed on rinsing. It is worth noting that although the physical properties of these films have changed over a period of time their d-spacings are virtually unchanged. The d-spacings of films 1, 7, 10, 14, 16B and 17 after four months soaking in
30   water are 14.0 Å, 14.0 Å 15.0 Å, 17.2 Å, 17.2 Å and 17.9 Å respectively. The biggest difference between previous measurements and the post-soaking results lie in film 10, which shows a change of nearly 0.6 Å.

35   Direct Evidence of Polymerization.

After extraction of the treated clays (treatments 1, 7, 10, 11, 14, 15, 20, 25, 28, 36, 40 and 42) with chloroform, fast atom bombardment (FAB) mass spectrometry indicates that

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polymerization of the additives has occurred. However, it is
also likely that most of the extracted material is derived from
surface polymerization since the d-spacings between the clay
galleries do not alter upon extraction. It is nevertheless
5 indicative that polymerization must be occurring within the clay
galleries.

The most definitive evidence for polymerization has been
obtained by solid-state nmr studies using laponite, subjected to
10 treatments 1 and 7 (Table 1). Magic-angle ^{13}C NMR clearly shows
that all formaldehyde has been polymerised in both samples. For
the sample from treatment 1 (BNH2 and FS), three major signals
are found at $\delta 15$, 47 and a large broad peak centred at δ 70
(covering 25 ppm). The highest field signal is due to the methyl
15 C's, while the remaining signals are due to aminal, methylene
and methine carbons. This convincing evidence for polymerisation
within the clay was repeated with the sample obtained from
treatment 7 (EDA and FS), with peaks at $\delta 34$, 45, 54, 67 and 167.
The most interesting peak (at 176 ppm) is indicative of either
20 imine or imminium ion formation. The remaining peaks are
consistent with EDA methylene C's, aminal C's, poly-acetal C's
(from poly-formaldehyde), and mixed hemi-aminal systems.

In the following the results of two further tests are described
25 examining quantitatively the effect of the disclosed method on
the clay material:

Cuttings Hardness Tests

30 Oxford Clay cuttings of between 2 and 4 mm diameter were soaked
in the test fluids under static, ambient temperature conditions
for 48 hrs. At the end of this period the cuttings were removed
from the solution by sieving and placed in the test device.
This consisted of a steel plate with an array of holes drilled
35 in it. The cuttings were forced through the holes by a piston
attached to a screw thread. Data were recorded as torque on the
screw thread against number of turns as the cuttings were

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extruded. A higher torque value indicates greater clay
inhibition.

FIG 1. shows the cuttings hardness data for the combinations of
5 DAP, DEC, EDA, BNH2 and Glyoxal, together with the corresponding
results for each of the components on its own in water. With
the exception of EDA + DEC, the performance of the combinations
was significantly superior to that of the individual components.

10

Permeability of Shale

An Oxford Clay core was used to assess the effect of one of the
reactive chemistries on permeability. The cylindrical core
15 approximately 25 mm in diameter and 30 mm long was confined in a
Hassler cell at a pressure of 8.5 MPa. One end of the core was
exposed to fluid at 8.0 MPa and fluid samples were collected
from the other end at atmospheric pressure to determine flowrate
and therefore permeability.
20

To establish an initial permeability for the untreated core it
was first exposed to a synthetic pore fluid. Once a stable flow
rate was established this fluid was switched over to the
reactive chemistry, BNH2 and Glyoxal, at 5wt% each in 0.1M $CaCl_2$
25 and adjusted to pH 9. FIG 2 shows the resulting change in
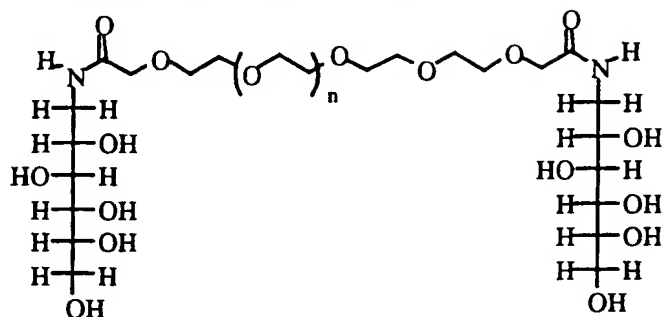permeability as the reaction progresses through the core.

CLAIMS

1.   A method of stabilizing a clayey geological formation
5   surrounding a hydrocarbon well comprising the step of
     injecting from a surface reservoir a fluid comprising a
     first and a second reactant, letting said fluid contact
     said clayey formation; and stabilizing said formation by
     using a reaction between said first and said second
10   reactant, wherein said reaction of said first and said
     second reactant is essentially initiated in the presence of
     said clayey material.

2.   The method of claim 1, wherein the reaction is
15   characterized by substrate intercalation or condensation
     stabilization with or without pH adjustment or
     stabilization through epoxide ring opening under neutral or
     acidic conditions or substrate in-situ polymerization or a
     combination thereof.
20
3.   The method of claim 1, wherein the first reactant is a
     diamine or a polyhydric alcohol and the second reactant
     comprises at least one carbonyl group.

25 4.   The method of claim 1, wherein the first reactant is a
     diamine or a dihydric alcohol and the second reactant
     comprises at least one carbonyl group.

5.   A method of drilling a wellbore into a potentially
30   hydrocarbon bearing formation comprising the steps of
     drilling part of said wellbore through a clayey formation
     and using a method in accordance with claim 1 to stabilize
     said formation.

Appendix 1. List of abbreviations.

.A   Acrolein

AA   Adipic acid

BA   Boric acid

BNH$_2$ CH$_3$CH(NH$_2$)CH$_2$-[OCH(CH$_3$)CH$_2$]$_1$-[OCH$_2$CH$_2$]$_m$-[OCH$_2$CH(CH$_3$)]$_n$-NH$_2$

B2P   2-^{t}Butylphenol

B4P   4-^{t}Butylphenol

DAP   1,5-Diaminopentane

DEA   Diethanolamine

DEC   Diethylcarbonate

DEM   Dimethylmalonate

DEO   Diethyloxalate

DIT   Diisopropyl-D-tartrate

DMM   Dimethylmaleate

EA   Ethanolamine

EDA   Ethylene-1,2-diamine or 1,2-diaminoethane

EG   Ethylene glycol

EPP   1,2-Epoxy-3-phenoxypropane

FS   37 % w/v Formaldehyde solution

GA   50% w/v Glutaric aldehyde solution

HQ   Hydroquinone

MA   Methyl acrylate

OA   Oxalic acid

P   Phenol

PA   2-Acetylpyridine

PC   2-Pyridinecarboxaldehyde
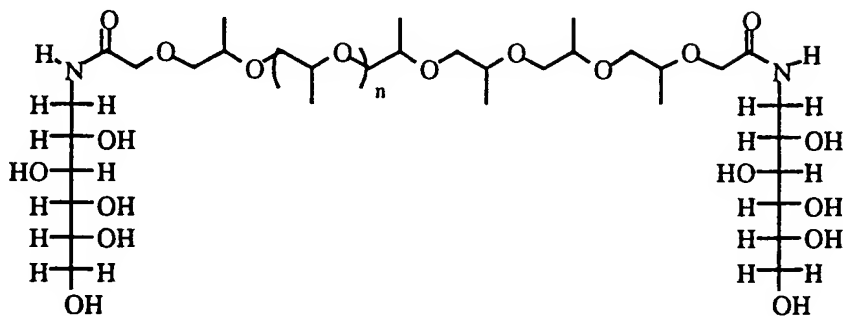
PO   Propylene oxide
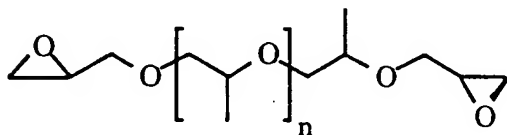
PEDG   Polyethylenediglucamide

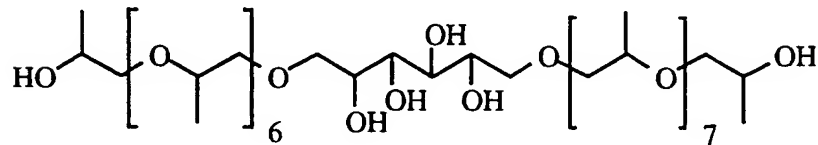PPD   1,2 Propanediol

PPDG   Polypropylenediglucamide

PPDGE

PEG

Appendix 2.

Table 1 (Properties of clay nanocomposite materials synthesized)

Film	Intercalator	Cross-linker	pH	d-spacing (Å)	Exfoliates	Stable	Brittle	Flexible	Hard or Soft
1	BNH2	FS	na	14.0		Yes		Yes	Hard
2	BNH2	MA/H2O2	na	-	Yes		Yes		Hard
3	BNH2/PEG	-	na	-			Yes		Hard
4	PEG	MA	na	-	Yes				Soft
5	PEG	MA/H2O2	na	-	Yes	Yes			Soft
6	PEG	BA	na	-	Yes				Soft
7	EDA	FS	na	14.4		Yes		Very	Hard
8	FS	Catalytic H2O2	na	-	Yes	Yes	Yes		Hard
9	EDA	PPDGE	6	-		Yes	Yes	Some	
10	EDA	EPP	6	15.6		Yes	Yes	Yes	Hard
11	EDA	PO	6	-		Yes		Yes	
12⁺	EDA	A	na	-					
13	BNH2	PPDGE	6	-	Yes	Yes	Yes		Hard
14	BNH2	EPP	6.4	-		Yes		Yes	Hard
15	BNH2	PO	6.6	-		Yes	Yes	Some	Hard
16B	4PEG:1BNH2	EPP	4	17.3		Yes		Yes	Hard
17	4PEG:1EDA	EPP	5	17.7		Yes	Slightly	Yes	Hard
18	PEG	EPP	na	-	Yes				Soft
19	PEG	PO	na	-	Yes				Soft
20	-	Styrene/H2O2	na	-	Yes				Soft
21	PEG	EPP/H2O2	na	-	Yes				Soft
22	PEG	PO/H2O2	na	-					Soft
23	DAP	FS	na	-		Yes	Yes		Hard
24	DAP	-	na	-		Yes		Yes	Hard
25	DAP	EPP	6.5	18.6		Yes	Slightly		Hard
26	DAP	PO	6.5	-		Yes	Yes		Hard
27	DAP	PO/EPP	na	17.2		Yes	Yes		Hard
28	EDA	PPDGE	2	14.1		Yes		Yes	Hard
29	BNH₂	PPDGE	2	15.9		Yes	Yes		Hard
30	PEG	PPDGE	2	17.5		Yes		Yes	Soft
31	PEG	PO	2	16.5	Yes	Yes			Soft

Table 1 (continued)

Film	Intercalator	Cross-linker	pH	d-spacing (Å)	Film Stability			Film Condition	
					Exfoliates	Stable	Brittle	Flexible	Hard or Soft
32	PEG	EPP	2	16.8	Yes	Yes			Soft
33	EDA	A	na	15.1		Yes		Yes	Hard
34	EDA	PC	na	17.7		Yes		Yes	Hard
35	EDA	PA	na	15.1		Yes			Hard
36*	EDA	AA	6	12.7		Yes		Yes	Hard
37	EDA	AA	na	15.0		Yes		Very	Hard
38*	EDA	AA	2	13.0		Yes		Yes	Hard
39*	EDA	OA	6	15.5		Yes	Yes	Slightly	Hard
40	EDA	OA	na	15.1		Yes		Very	Hard
41*	EDA	OA	2	15.6		Yes		Yes	Hard
42	EDA	GA	na	15.5		Yes		Yes	Hard
43	BNH$_2$	GA	na	-∞	Yes	Yes		Yes	
44	PEDG	PO	6	-	Yes				
45	PEDG	EPP	6	-	Yes				
46	PEDG	PDGE	6	-	Yes				
47	PPDG	PO	6	-	Yes				
48	PPDG	EPP	6	-	Yes				
49	PPDG	PDGE	6	-	Yes				
50	EDA	DEC	na	-		Yes		Very	Hard
51	BNH$_2$	DEC	na	-		Yes	Yes		Hard
52	DAP	DEC	na	-		Yes		Very	Hard
53	EA	DEC	na	-		Yes		Yes	Hard
54	DEA	DEC	na	-		⊥			Soft
55	EG	DEM	na	-	Yes	⊥			Soft
56	EG	DMM	na	-	Yes	⊥			Soft
57	EG	DIT	na	-	Yes	Yes		Yes	
58	EG	DEO	na	-	Yes	Yes1		Yes	
59	PPD	DEM	na	-	Yes				Soft
60	PPD	DMM	na	-	Yes	⊥			Soft
61	PPD	DIT	na	-	Yes			Yes	Soft
62	PPD	DEO	na	-	Yes	⊥			Soft
63	HQ	FS	na	-		Yes		Yes	Hard
64	P	FS	na	-	Some	Yes		Yes	Hard

65	B4P	FS	na	-		Yes		Yes	Yes	Hard
66	B2P	FS	na	-	Yes	Yes	Slightly	Yes	Yes	Hard

+ film 12 test resulted in polymerisation of the intercalator solution on addition of the acrolein

* considerable precipitation of intercalator/cross-linker complex

ω although film 43 is stable no d-spacing was measured due to the non-homogeneous nature of the treated film

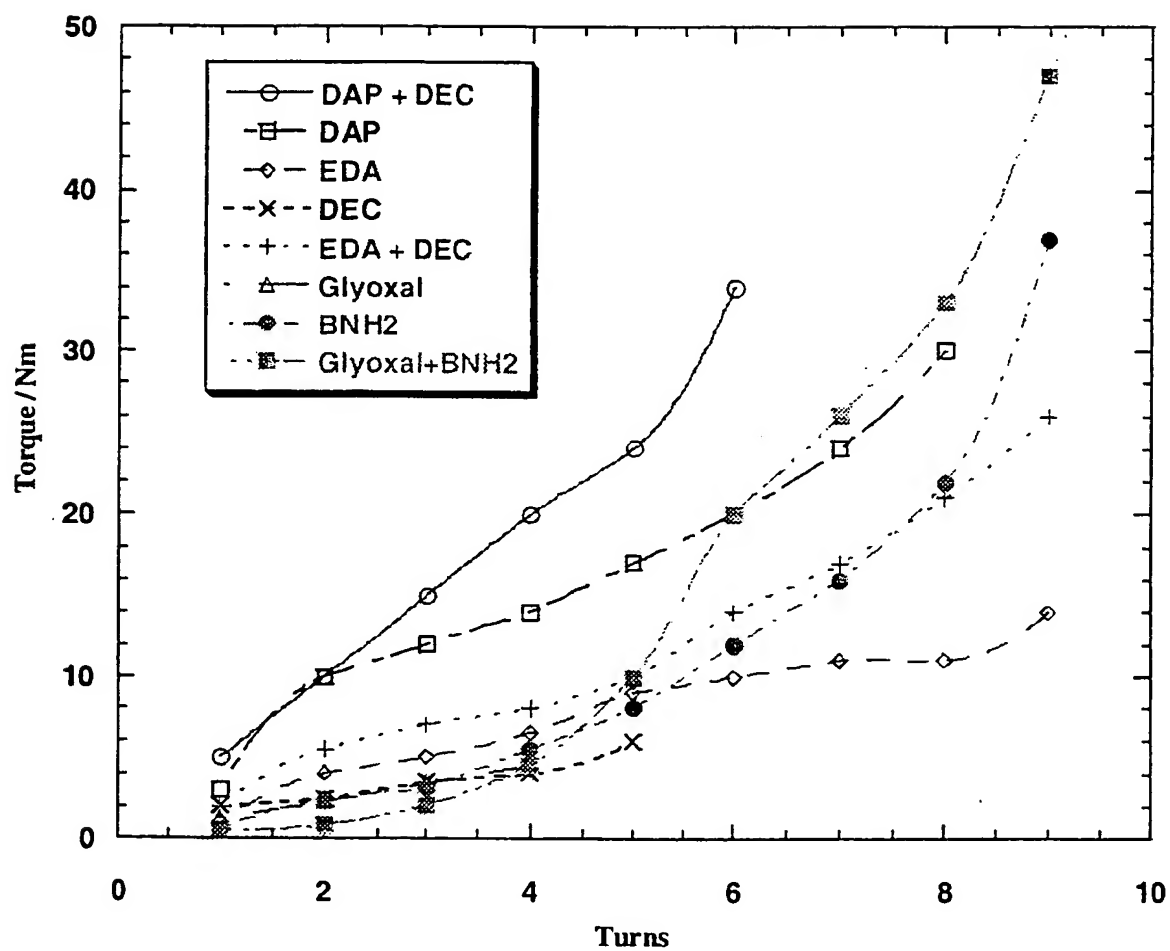⊥ All these films decompose upon overnight soaking in fresh water

FIG. 1
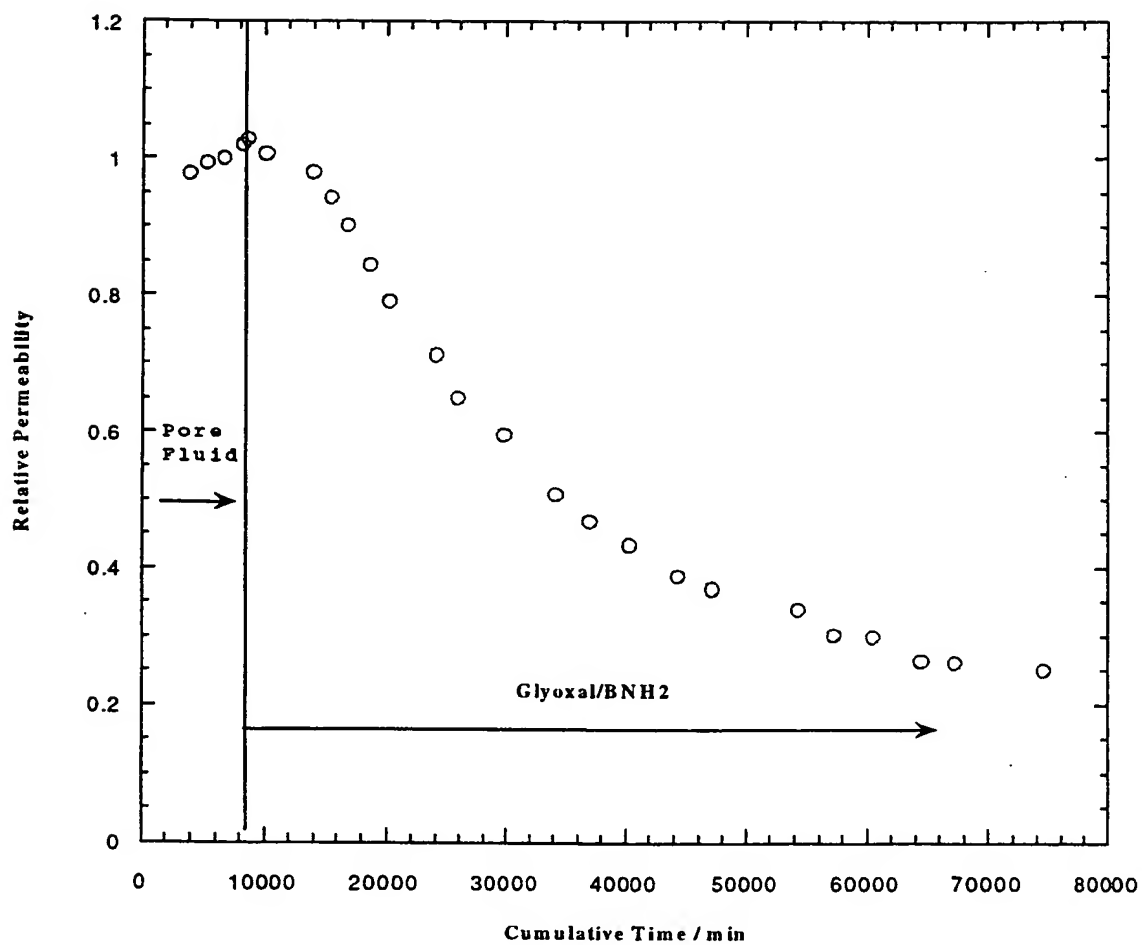
FIG. 2

INTERNATIONAL SEARCH REPORT

Inter onal application No.

PCT/GB 98/03700

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: E21B 43/25, E21B 43/22, E21B 33/138

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: E21B, C09H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5099923 A (C.W. AFTEN ET AL), 31 March 1992 (31.03.92) --	1-5
A	US 4828726 A (R.E. HIMES ET AL), 9 May 1989 (09.05.89) --	1-5
A	EP 0308138 A1 (HALLIBURTON COMPANY), 22 March 1989 (22.03.89) --	1-5
A	US 4693639 A (K.H. HOLLENBEAK ET AL), 15 Sept 1987 (15.09.87) -- --------	1-5

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
9 March 1999	0 8. 04. 99

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INTERNATIONAL SEARCH REPORT
Information on patent family members

| 02/02/99 | International application No. |
| | PCT/GB 98/03700 |

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			EP 0251558 A		07/01/88